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WO 01/92242 A1

(54) **Title:** PROCESS FOR MANUFACTURING AN OXIRANE

(57) **Abstract:** Process for manufacturing an oxirane, in which an olefin is reacted, in a diluent chosen from water, alcohols and ketones, with a peroxide compound in the presence of a catalyst and in the presence of a compound comprising an aminocarbonyl function in which the nitrogen atom bears at least one hydrogen atom.

Process for manufacturing an oxirane

The invention relates to a process for manufacturing an oxirane by reaction between an olefin and a peroxide compound in the presence of a catalyst and a diluent. The invention relates more particularly to a process for manufacturing 1,2-epoxypropane (propylene oxide) or 1,2-epoxy-3-chloropropane (epichlorohydrin) by reaction between propylene or allyl chloride and hydrogen peroxide.

It is known practice to manufacture propylene oxide by epoxidation of propylene using hydrogen peroxide in a solvent and in the presence of a catalyst of TS-1 type, as disclosed, for example, in patent application EP-A-0 568 336. Methanol is used as solvent in the examples.

This known process has the drawback of resulting in the formation of by-products. Specifically, when propylene oxide is manufactured, by-products are formed by reaction between the propylene oxide and water or methanol, and in particular propylene glycol and methoxypropanols of formulae CH_3-CHOH-CH_2-OCH_3 and CH_3-CH(OCH_3)-CH_2OH. When epichlorohydrin is manufactured, by-products are formed by reaction between the epichlorohydrin and water or methanol, and in particular 1-chloropropanediol and chloromethoxypropanols of formulae $ClCH_2$-CHOH-CH_2-OCH_3 and Cl-CH_2-CH(OCH_3)-CH_2OH. The formation of by-products reduces the selectivity of the process and consequently its yield.

In patent application EP-A-0 940 393, it is proposed to reduce the formation of by-products using an amide whose nitrogen atom bears two substituents.

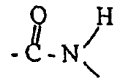
The invention is directed towards providing an alternative process for preventing the formation of by-products which makes it possible to obtain an even higher selectivity, while at the same time maintaining the highest possible activity (or reaction rate).

The invention consequently relates to a process for manufacturing an oxirane, in which an olefin is reacted, in a diluent chosen from water, alcohols and ketones, with a peroxide compound in the presence of a catalyst and in the presence of a compound comprising an aminocarbonyl function in which the nitrogen atom bears at least one hydrogen atom.

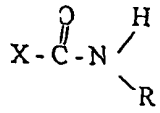
One of the essential characteristics of the invention lies in the presence of the compound comprising an aminocarbonyl function in the epoxidation medium. Specifically, it has been found that the presence of such a compound, even at low content, makes it possible to greatly reduce the formation of by-products such as methoxypropanols. For example, by adding such a compound to the epoxidation medium, the amount of by-products formed may be reduced when compared with a process performed under identical conditions but in the absence of the said compound, by at least 20%, in particular by at least 30%, preferably by at least 50%. In certain cases, the amount of by-products may be reduced by at least 75%. A selectivity towards epoxide, expressed by the molar ratio of the epoxide formed to the sum of the by-products (expressed as C3) plus the epoxide, of at least 75%, in particular of at least 80% and preferably of at least 85%, may thus be expected, a selectivity of at least 90% being particularly preferred.

The amount of compound comprising an aminocarbonyl function used in the process according to the invention may vary within a wide range. Very low doses already have a significant effect on the formation of by-products. Excessively large amounts may not be desirable in certain cases since they result in a reduction of the reaction rate. In general, a good compromise between the rate and the selectivity is obtained with a molar ratio of the amounts of the said compound and of diluent used of at least 0.001%. This ratio is in particular at least 0.005% and preferably at least 0.01%. A ratio of at least 0.1% gives the best results. The ratio is usually not more than 50%, for example less than 34%, in particular not more than 30%. A ratio of not more than 10% is preferred. A ratio of not more than 5% gives good results.

The expression "compound comprising an aminocarbonyl function whose nitrogen atom bears at least one hydrogen atom" is intended to denote compounds comprising a group of formula



The compound comprising an aminocarbonyl function which is used in the process according to the invention may be chosen from compounds corresponding to the formula



in which:

- X may be $-NH_2$, $-NHY$, $-NY_2$ or Y;
- R and Y are identical or different;
- R and Y may be chosen from hydrogen and a radical preferably containing from 1 to 20 carbon atoms. This radical may be of the alkyl (preferably containing from 1 to 20 carbon atoms), aryl or alkylaryl (preferably containing from 6 to 20 carbon atoms), cycloalkyl (preferably containing from 5 to 20 carbon atoms) or heterocyclic (preferably containing from 5 to 20 carbon atoms and one or more heterogeneous atoms chosen from N, O and S) type. Preferably, R contains no carbonyl function;
- X and R may form a saturated or unsaturated ring optionally comprising one or more heterogenous atoms chosen from N, O and S.

Preferably, X is chosen from $-NH_2$ and alkyl radicals containing from 1 to 6 and in particular from 1 to 3 carbon atoms. R is preferably hydrogen or an alkyl radical containing from 1 to 6 and preferably from 1 to 3 carbon atoms. Preferably, the compound contains only one carbonyl function. Examples which may be mentioned are acetamide, urea and N-methylacetamide. Urea is suitable for use. Compounds which form an azeotrope with the diluent have the advantage of being easy to recycle with the diluent.

The diluent used in the process according to the invention may be chosen from linear or branched, saturated aliphatic alcohols. The alcoholic diluent generally contains up to 10 carbon atoms, preferably from 1 to 6 carbon atoms. Examples which may be mentioned are methanol and ethanol. Methanol is preferred.

The epoxidation medium in which the olefin reacts with the peroxide compound in the presence of the catalyst, the alcoholic diluent and the compound comprising an aminocarbonyl function usually also contains water. The epoxidation medium generally comprises a liquid phase, a gaseous phase and the catalyst in solid form. The liquid phase contains the diluent, the compound comprising an aminocarbonyl function, the dissolved olefin, the peroxide compound, a fraction of the epoxide formed and water.

The total amount of diluent and of compound comprising an aminocarbonyl function used in the process according to the invention is generally at least 35% by weight of the liquid phase defined above, in particular at least 60% by weight, for example at least 75% by weight. This amount usually does not exceed 99% by weight and in particular does not exceed 95% by weight.

The molar ratio between the amounts of olefin and of peroxide compound used in the process according to the invention is generally at least 0.1, in particular at least 1 and preferably at least 5. This molar ratio is usually not more than 100, in particular not more than 50 and preferably not more than 25.

The process according to the invention may be continuous or batchwise.

In the process according to the invention, when it is performed continuously, the peroxide compound is generally used in an amount of at least 0.005 mol per hour and per gram of catalyst, in particular of at least 0.01 mol per hour and per gram of catalyst. The amount of peroxide compound is usually less than or equal to 2.5 mol per hour and per gram of catalyst and in particular less than or equal to 1 mol per hour and per gram of catalyst. Preference is shown for an amount of peroxide compound of greater than or equal to 0.03 mol per hour and per gram of catalyst and less than or equal to 0.25 mol per hour and per gram of catalyst.

In the process according to the invention, the peroxide compound is advantageously used in the form of an aqueous solution. In general, the aqueous solution contains at least 10% by weight of peroxide compound, in particular at least 20% by weight. It usually contains not more than 70% by weight of peroxide compound, in particular not more than 50% by weight.

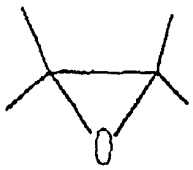
The temperature of the reaction between the olefin and the peroxide compound may range from 10°C to 100°C. In one advantageous variant, it is greater than 35°C in order to overcome the gradual deactivation of the catalyst. The temperature may be greater than or equal to 40°C and preferably greater than or equal to 45°C. A temperature of greater than or equal to 50°C is most particularly preferred. The reaction temperature is preferably less than 80°C.

In the process according to the invention, the reaction between the olefin and the peroxide compound may take place at atmospheric pressure. It may also take place under pressure. This pressure generally does not exceed 40 bar. A pressure of 20 bar is suitable in practice.

The peroxide compounds which may be used in the process according to the invention are peroxide compounds containing one or more peroxide functions (-OOH) which may release active oxygen and which are capable of carrying out an epoxidation. Hydrogen peroxide and peroxide compounds which may produce hydrogen peroxide under the conditions of the epoxidation reaction are suitable for use. Hydrogen peroxide is preferred.

When hydrogen peroxide is used, it may be advantageous to use an aqueous hydrogen peroxide solution in crude form, i.e. in unpurified form, in the process according to the invention. For example, a solution obtained by simple extraction, with substantially pure water, of the mixture derived from the oxidation of at least one alkylanthrahydroquinone (process known as "autoxidation AO process") may be used without a subsequent washing and/or purification treatment. These crude hydrogen peroxide solutions generally contain from 0.001 to 10 g/l of organic impurities expressed as TOC (Total Organic Carbon). They usually contain metal cations (such as alkali metals or alkaline-earth metals, for instance sodium) and anions (such as phosphates or nitrates) in contents of from 0.01 to 10 g/l.

The oxirane which may be prepared by the process according to the invention is an organic compound comprising a group corresponding to the general formula :



The oxirane generally contains from 2 to 10 carbon atoms, preferably from 3 to 6 carbon atoms. The oxiranes which may be prepared advantageously by the process according to the invention are 1,2-epoxypropane and 1,2-epoxy-3-chloropropane.

The olefins which are suitable for use in the process according to the invention generally contain from 2 to 10 carbon atoms and preferably 3 to 6 carbon atoms. Propylene, butylene and allyl chloride are suitable for use. Propylene and allyl chloride are preferred.

The catalyst used in the process according to the invention generally contains a zeolite. The catalyst contains in most cases titanium. Usually, a titanium zeolite is used. The term "titanium zeolite" is intended to denote a solid containing silica which has a microporous crystal structure of zeolite type and in which several silicon atoms are replaced with titanium atoms. The catalysts advantageously have a crystal structure of ZSM-5, ZSM-11 or MCM-41 type. They may also have a crystal structure of β zeolite type. The catalyst is usually free of aluminium. It preferably has an infrared adsorption band at about 950-960 cm^{-1}. Catalysts corresponding to the formula $xTiO_2(1-x)SiO_2$ in which x is from 0.0001 to 0.5 and preferably from 0.001 to 0.05 give good results. Materials of this type, known under the name TS-1, give high-quality performance.

In the process according to the invention, a gas which has no negative effect on the epoxidation reaction may also be added to the reactor. Specifically, in patent application WO 99/48883 (the content of which is incorporated by reference into the present patent application), the Applicant has found that by introducing a gaseous compound into the reaction medium at a flow rate which is sufficient to allow the oxirane produced to be entrained and to removed from the reactor at the same time as the gaseous compound, the contact time between the oxirane produced and the epoxidation reaction medium is reduced. The formation of by-products is thus also prevented and the selectivity towards epoxidation is increased.

In the process according to the invention, any type of reactor may be used, in particular a reactor of loop type. Reactors of loop type with a bubble siphon, in which the circulation of the liquid and optionally also of the catalyst is obtained by bubbling a gas through one of the arms, are particularly suitable. This type of reactor is disclosed in the patent application WO 99/48883 mentioned above.

In the process according to the invention, it may prove to be advantageous to monitor the pH of the liquid phase. For example, it may be advantageous to maintain the pH of the liquid phase during the reaction between the olefin and the peroxide compound at a value of from 4.8 to 6.5, for example by adding a base (sodium hydroxide) to the epoxidation medium, as recommended in patent application WO 99/48882 by the Applicant (the content of which is incorporated by reference into the present patent application).

The reaction between the olefin and the peroxide compound may be carried out in the presence of a salt such as sodium chloride, as disclosed in patent

application WO EP 99/08703 by the Applicant (the content of which is incorporated by reference into the present patent application).

It may be advantageous to introduce the olefin into the reactor, in which the epoxidation reaction takes place, in a form diluted in one or more alkanes. For example, a fluid containing the olefin and also at least 10% (in particular 20%, for example at least 30%) by volume of one or more alkanes may be introduced into the epoxidation reactor. For example, in the case of propylene, the latter may be mixed with at least 10% by volume of propane when recycled unconverted propylene is introduced into the reactor. It may also be a source of propylene which is not completely freed of propane.

Example 1 (reference)

3 g of TS-1 and 115 g of methanol (3.6 mol) are introduced into a jacketed Pyrex reactor with a volume of 200 ml, equipped with a stirrer and on which is mounted a condenser cooled to –20°C. The temperature is set at 25°C. Propylene is then introduced at a flow rate of 18 Nl/h via a sintered tube. After flushing for 30 minutes with propylene (Pe), 22.25 g of a 34.4 wt% hydrogen peroxide solution (225 mmol) are added over 20 min.

The hydrogen peroxide content is monitored and determined by iodometry. Its change makes it possible to calculate a rate constant (first order relative to hydrogen peroxide). When the degree of conversion of the hydrogen peroxide reaches 85%, the liquid phase containing the propylene oxide and the by-products (methoxypropanols "MeOPols" and propylene glycol "Diol") is analysed by gas chromatography to determine the selectivity. The selectivity is defined as the ratio between the propylene oxide formed and the sum of the organic products collected (propylene oxide + by-products). The results are collated in Table 1.

Examples 2 to 4 (in accordance with the invention)

The process is performed as in Example 1, except that the solvent consists of a mixture of methanol (MeOH) and of a compound comprising an aminocarbonyl function in accordance with the invention (acetamide in Example 2, N-methylacetamide in Example 3 and urea in Example 4). The results are collated in Table 1.

Examples 5 to 9 (not in accordance with the invention)

The process is performed as in Example 1, except that the solvent consists of a mixture of methanol (MeOH) and of an amide disclosed in patent application EP-A-0 940 393 (N,N-dimethylacetamide in Example 5,

N,N-dimethylformamide in Examples 6 and 7, and N-methylpyrrolidone in Examples 8 and 9). The results are collated in Table 1.

Table 1

Ex.	Compound comprising an aminocarbonyl function	MeOH/compound molar ratio	Selectivity towards epoxide at 85% conversion of H_2O_2 (mol%)	Rate constant (min^{-1})
1	-	100/0	89.33	0.064
2	Acetamide	99/1	96.11	0.051
3	N-Methyl-acetamide	99/1	96.35	0.052
4	Urea	99/1	97.58	0.040
5	N,N-Dimethyl-acetaminde	99/1	96.17	0.033
6	N,N-Dimethyl-formamide	99/1	(a)	0.004
7	N,N-Dimethyl-formamide	99.75/0.25	96.91	0.014
8	N-Methyl-pyrrolidone	99/1	(a)	0.005
9	N-Methyl-pyrrolidone	99.75/0.25	96.51	0.017

(a): an 85% conversion of the hydrogen peroxide was not achieved even after a reaction time of 120 min.

CLAIMS

1 - Process for manufacturing an oxirane, in which an olefin is reacted, in a diluent chosen from water, alcohols and ketones, with a peroxide compound in the presence of a catalyst and in the presence of a compound comprising an aminocarbonyl function in which the nitrogen atom bears at least one hydrogen atom.

2 - Process according to Claim 1, in which the molar ratio of the amounts of compound comprising an aminocarbonyl function and of diluent used is at least 0.001% and not more than 50%.

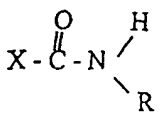
3 - Process according to Claim 2, in which the molar ratio of the amounts of compound comprising an aminocarbonyl function and of diluent used is at least 0.01% and not more than 10%.

4 - Process according to claim 3, in which the molar ratio of the amounts of compound comprising an aminocarbonyl function and of diluent used is at least 0,1 %.

5 - Process according to any one of the preceding claims, in which the total amount of diluent and of compound comprising an aminocarbonyl function used is at least 35% and not more than 99% by weight of the liquid phase containing the diluent, the said compound, the dissolved olefin, the peroxide compound, a fraction of the oxirane formed and water.

6 - Process according to claim 5, in which the total amount of diluent and of compound comprising an aminocarbonyl function used is at least 60 % by weight of the liquid phase.

7 - Process according to any one of the preceding claims, in which the compound comprising an aminocarbonyl function is chosen from the compounds corresponding to the formula



in which:

- X may be $-NH_2$, $-NHY$, $-NY_2$ or Y;
- R and Y are identical or different;
- R and Y may be chosen from hydrogen and a radical preferably containing from 1 to 20 carbon atoms;
- X and R may form a saturated or unsaturated ring optionally comprising one or more heterogenous atoms chosen from N, O and S;

and the diluent is chosen from among the saturated, linear or branched aliphatic alcohols.

8 - Process according to Claim 7, in which the compound comprising an aminocarbonyl function is chosen from acetamide, urea and N-methylacetamide.

9 - Process according to Claim 8, in which the compound comprising an aminocarbonyl function is urea and the diluent is methanol.

10 - Process according to any one of the preceding claims, in which the olefin reacts with the peroxide compound in the presence of the catalyst, the diluent and the compound comprising an aminocarbonyl function at a temperature of from 10°C to 100°C and at a pressure which can range from atmospheric pressure to 40 bar.

11 - Process according to any one of the preceding claims, in which the oxirane is 1,2-epoxypropane, the olefin is propylene and the peroxide compound is hydrogen peroxide.

12 - Process according to any one of Claims 1 to 8, in which the oxirane is 1,2-epoxy-3-chloropropane, the olefin is allyl chloride and the peroxide compound is hydrogen peroxide.

13 – Process according to any one of claims 1 to 12, in which the reaction of the olefin with the peroxide compound is carried out in the presence of water.

14 – Process according to any one of claims 1 to 13, in wich the catalyst contains titanium.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/05793

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D301/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 940 393 A (ENICHEM S.P.A.) 8 September 1999 (1999-09-08) cited in the application the whole document	1-14
Y	FR 2 082 811 A (INSTITUT FRANÇAIS DU PÉTROLE, DES CARBURANTS ET LUBRIFIANTS) 10 December 1971 (1971-12-10) the whole document	1-14
Y	US 5 723 636 A (STEVEN P. FENELLI) 3 March 1998 (1998-03-03) the whole document	1-14
Y	DD 122 379 A (FRANZ, DIPL.-CHEM. KARL) 5 October 1976 (1976-10-05) the whole document	1-14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
6 September 2001	14/09/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Beslier, L

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INTERNATIONAL SEARCH REPORT

Interna[redacted]nal Application No
PCT/EP 01/05793

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,Y	EP 1 072 599 A (ENICHEM S.P.A.) 31 January 2001 (2001-01-31) the whole document -----	1-14

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern[redacted]nal Application No
PCT/EP 01/05793

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